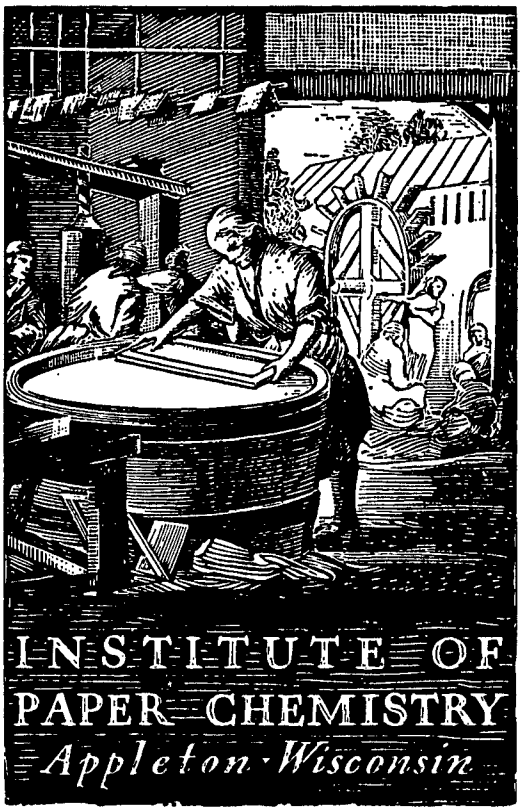


DEGRADATIVE CHANGES IN CARBOHYDRATES OF PULPS FROM OXYGEN-ALKALI REACTIONS

Project 3284

Report One

A Progress Report

to

MEMBERS OF THE INSTITUTE OF PAPER CHEMISTRY

August 27, 1976

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

DEGRADATIVE CHANGES IN CARBOHYDRATES OF PULPS FROM OXYGEN-ALKALI REACTIONS

Project 3284

Report One

A Progress Report

to

MEMBERS OF THE INSTITUTE OF PAPER CHEMISTRY

August 27, 1976

TABLE OF CONTENTS

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

DEGRADATIVE CHANGES IN CARBOHYDRATES OF PULPS FROM OXYGEN-ALKALI REACTIONS

SUMMARY

Oxygen-alkali red maple (Acer rubrum) pulps and the corresponding spent liquors are being analyzed to determine what changes occur in the wood carbohydrates during the pulping process. The pulps, prepared as part of a concurrent pulping study, were generated under both low and high consistency conditions using oxygen-sodium carbonate-sodium bicarbonate and oxygen-sodium carbonate, respectively.

Neutral sugar analyses of the pulps by the alditol acetate method indicate that both pulping processes selectively remove lignin relative to the carbohydrates, but that the degree of selectivity is not very great. The degree of selectivity may be somewhat greater in the low consistency process. The carbohydrate loss in both processes is due primarily to loss of hemicelluloses; loss of cellulose is minimal down to the 65% yield level. Magnesium carbonate at 1% loading (o.d. wood basis) did not affect carbohydrate retention in the high consistency process. Potassium iodide at 10% loading increased carbohydrate retention by 2-3% in the high consistency process.

Ultrafiltration is being used to assess the molecular size of the solids in pulping spent liquors. The ultrafiltration analyses, in conjunction with neutral sugar analyses of the fractionated solids, indicate that a major portion of the polysaccharides removed from the pulp in the high consistency process is degraded to low molecular weight (<1000) species. Magnesium carbonate did not have an appreciable effect on the degradation.

Gel permeation chromatographic analysis of the carbanilate derivatives of the pulp holocelluloses is being assessed as a method for determining changes in the degree of polymerization of the wood polysaccharides during pulping. The method appears to be feasible if degradation, which occurs during derivatization of the holocellulose, can be circumvented or minimized.

INTRODUCTION

In initiating a research program to investigate the potential of producing high yields of pulp with desirable papermaking properties by delignification of wood with oxygen in alkaline media (Project 3264, Oxidative Delignification with Oxygen/Alkali to High-Yield Pulps), it was thought that incomplete knowledge of the basic wood chemistry related to such systems could be a problem (1). This research project was therefore initiated to determine what changes occur in the wood polysaccharides, and their relative importance, when wood is delignified under various conditions with oxygen in alkaline media (2).

Based on information available on reactions of carbohydrates in such systems, the primary concerns from the standpoint of material loss or degradation of the polysaccharides within the fiber are: (a) peeling, or end-wise degradation of the polysaccharides; (b) selective removal of hemicelluloses; (c) oxidation of the polysaccharides; and (d) depolymerization, or cleavage of glycosidic linkages of the polysaccharides (2).

The phenomenon of peeling in which monomeric units are sequentially eliminated from an unstabilized reducing end of a polysaccharide and subsequently form acidic products is well established as a source of material loss in alkaline treatments of wood or wood pulps (3-4). In addition, the structural characteristics of polysaccharides which permit peeling to occur are believed to be reasonably well understood (4-5). Thus, it can be anticipated that in alkaline media containing oxygen, cellulose and glucomannan will be susceptible to peeling until their reducing ends become stabilized either through the "normal stopping reaction" (4) or possibly through an accelerated "oxidative stopping reaction" (6-7). Xylans containing xylopyranose units substituted at C-2 or C-3 will be less susceptible to peeling degradation (4,8).

Limited analyses of oxygen-alkali spent liquors (9-10) indicate that hemicelluloses are selectively removed relative to cellulose in the process. In addition, the bulk of the dissolved hemicellulose is reported to be converted to organic acids (9).

In theory, each of the carbon atoms in a monosaccharide unit of wood polysaccharides can be oxidized. Oxygen-alkali pulps have higher carboxyl contents than kraft pulps (11) and higher carboxyl and carbonyl contents than soda pulps (12). These functional groups are thought to be located primarily in the lignin of oxygen-alkali pulps, since the amount of carbonyl and carboxyl groups decreases with decreasing lignin contents (12). However, a similar result would be obtained if oxidized hemicelluloses were attached to the lignin. Since carboxyl and carbonyl groups can significantly affect the physical and chemical properties of pulps (13-14), it is of interest to attempt to ascertain to what extent these functional groups are present in the wood polysaccharides.

The extent of depolymerization of the wood polysaccharides, particularly cellulose, in a pulp is related to potential paper strength. There are differences of opinion on how depolymerization, or chain cleavage, of polysaccharides occurs in oxygen-alkali. However, formation of carbonyl groups within the monosaccharide units and subsequent β-eliminations appears to be the commonly accepted reaction mechanism (15-17).

The initial emphasis of the project has been to ascertain which analytical procedures are appropriate for detecting and measuring the extent of the above general reactions. Many of the analytical procedures employed with simpler polysaccharide systems are not directly applicable to the wood saccharides because of the complicating effects of the associated lignin and the multicomponent nature of the wood polysaccharides.

RESULTS AND DISCUSSION

GENERAL

Materials utilized in the project have been prepared as an integral part of a concurrent oxygen-alkali pulping project, Project 3264 (1). The materials include fiberized red maple (Acer rubrum) chips (FRM) (18), fiberized chips which have been treated with sodium hydroxide (AT-FRM), pulps prepared at various yield levels at both high consistency (HC) standard conditions employing sodium carbonate as the base and low consistency (LC) standard conditions employing sodium carbonate and sodium bicarbonate, and pulps prepared using magnesium carbonate (Mg) and potassium iodide (KI) as degradation inhibitors.

Alkali pretreated fiberized chips (AT-FRM) were prepared by treating fiberized red maple chips (FRM) with 5% sodium hydroxide (o.d. FRM basis) at 10% consistency for 30 minutes at 90°C. The yield of AT-FRM was approximately 90%.

In the high consistency (HC) process a liquor-to-wood ratio of ca. 3:1 with ca. 25 g/liter sodium carbonate (Na_2CO_3) was used. The starting material for the process was AT-FRM. A reaction temperature of 120°C for 4 to 14 hours, with an oxygen pressure of 130 psig, provided yields ranging from ca. 80 to 65% (o.d. FRM basis), respectively.

In the low consistency (LC) process, a liquor-to-wood ratio of ca. 70:1 with ca. 7.5 g/liter sodium bicarbonate ($NaHCO_3$) and 10 g/liter sodium carbonate (Na_2CO_3) was used. The pulping liquor was continuously circulated through the starting material (FRM) which was held stationary. A reaction temperature of 120°C for 165 and 215 minutes with air pressure at 3000 psig resulted in yields of ca. 70 and 66% (o.d. FRM basis), respectively.

CARBOHYDRATE LOSSES IN OXYGEN-ALKALI PULPING

The amount of carbohydrate lost from wood or pulp during processing can be obtained from yield data for the process in conjunction with analyses of the sugars in the materials after hydrolysis of the polysaccharides. This type of analysis has been used quite successfully in determining the importance of carbohydrate losses in the low and high temperature regions of the kraft process (19). In addition, this type of analysis can indicate whether a particular type of polysaccharide is being selectively removed during processing.

Analytical Method

The monosaccharides in hydrolyzates of wood and pulps are most frequently analyzed by gas-liquid chromatography (GLC) as their alditol acetates utilizing an ECNSS-M (ethylenesuccinate-cyanoethylsilicone copolymer) GLC column (20-21). A GLC analysis of a standard mixture of alditol acetates with this type of column is illustrated in Fig. 1. In this study the alditol acetate method is being used for neutral sugar analyses, but an SP-2340 (3-cyanopropylsilicone) column is being utilized in the GLC analyses. As illustrated in Fig. 1, an SP-2340 column provides as good, if not better, resolution of the alditol acetates as an ECNSS-M column. However, the major advantage of the SP-2340 column packing is that it is considerably more stable than ECNSS-M which has a short effective lifetime at the necessary operating conditions. Thus far, all neutral sugar analyses for this study have been performed on a single SP-2340 column. A conservative estimate is that at least 130 analyses have been performed without a significant loss of column resolution.

Although, in theory, the analysis of neutral sugars of wood and pulps is relatively straightforward (20-21), problems are encountered with the analyses.

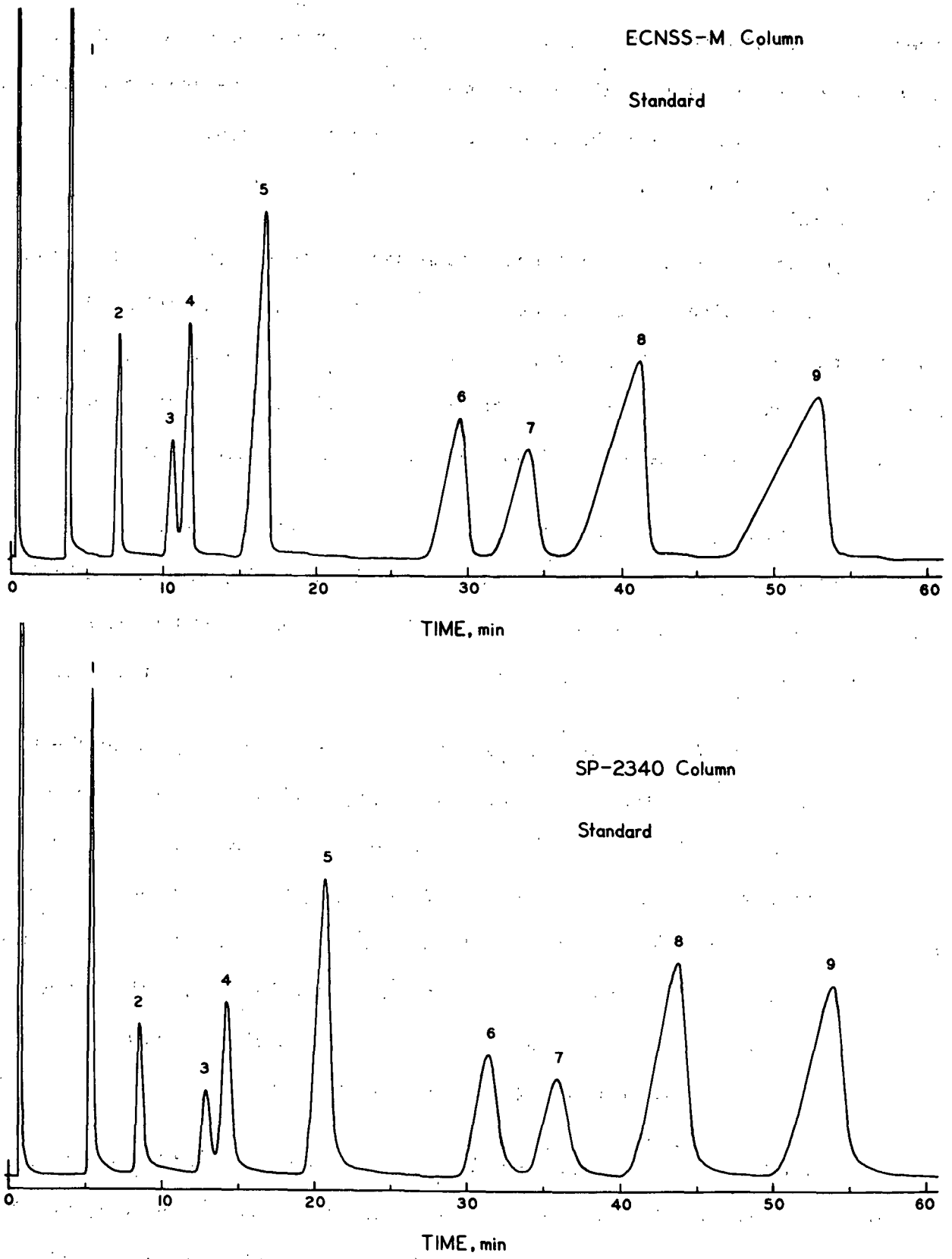


Figure 1. Gas-Liquid Chromatographic Analyses of a Standard Mixture of Alditol Peracetates: (1) Erythritol, (2) L-Rhamnitol, (3) Ribitol, (4) L-Arabinitol, (5) Xylitol, (6) D-Mannitol, (7) Galactitol, (8) D-Glucitol, and (9) myo-Inositol (Internal Standard)

Too frequently, inexplicable variation in replicate samples occur. One of the major variables in the analytical method appears to be the procedure for hydrolysis of the wood or pulp sample and the attendant neutralization step.

Wood and Pulp Analyses

Representative GLC chromatograms from neutral sugar analyses are shown in Fig. 2. One chromatogram is from an analysis of fiberized red maple chips (FRM), the other is from a 72% yield pulp (HC-72-Mg) prepared by the high consistency process using magnesium carbonate as an "inhibitor." Quantitative analyses of the neutral sugars of the wood and various pulps are reported in Table I.

The analysis of FRM reported in Table I is the average of replicate analyses. The average neutral glycan content of FRM was 65.0%, with a standard deviation of ± 1.0%. For comparison, an analysis of red maple (RM) previously reported by Timell (22) is also given in Table I. The analyses are quite similar.

Sodium hydroxide pretreatment of the fiberized chips to produce AT-FRM resulted in a 10% loss of material, approximately one-half of which was due to loss of carbohydrates. The differential should reflect loss of acetyl groups, extractives, and lignin. Subsequent losses of carbohydrate on subjecting AT-FRM to the high consistency process were significantly lower, accounting for only 20-30% of the material loss over the 65-80% yield range (see Table I). Thus, the process does selectively remove lignin, or conversely, selectively retain carbohydrates, but the degree of selectivity is not extremely great.

In the low consistency process in which FRM was the starting material, ca. 27% of the total material loss at the 66% yield level (LC-66, Table I) was due to loss of carbohydrates. On the same basis, the carbohydrate loss in the high consistency process was ca. 33% of the total material loss at the 66% yield level

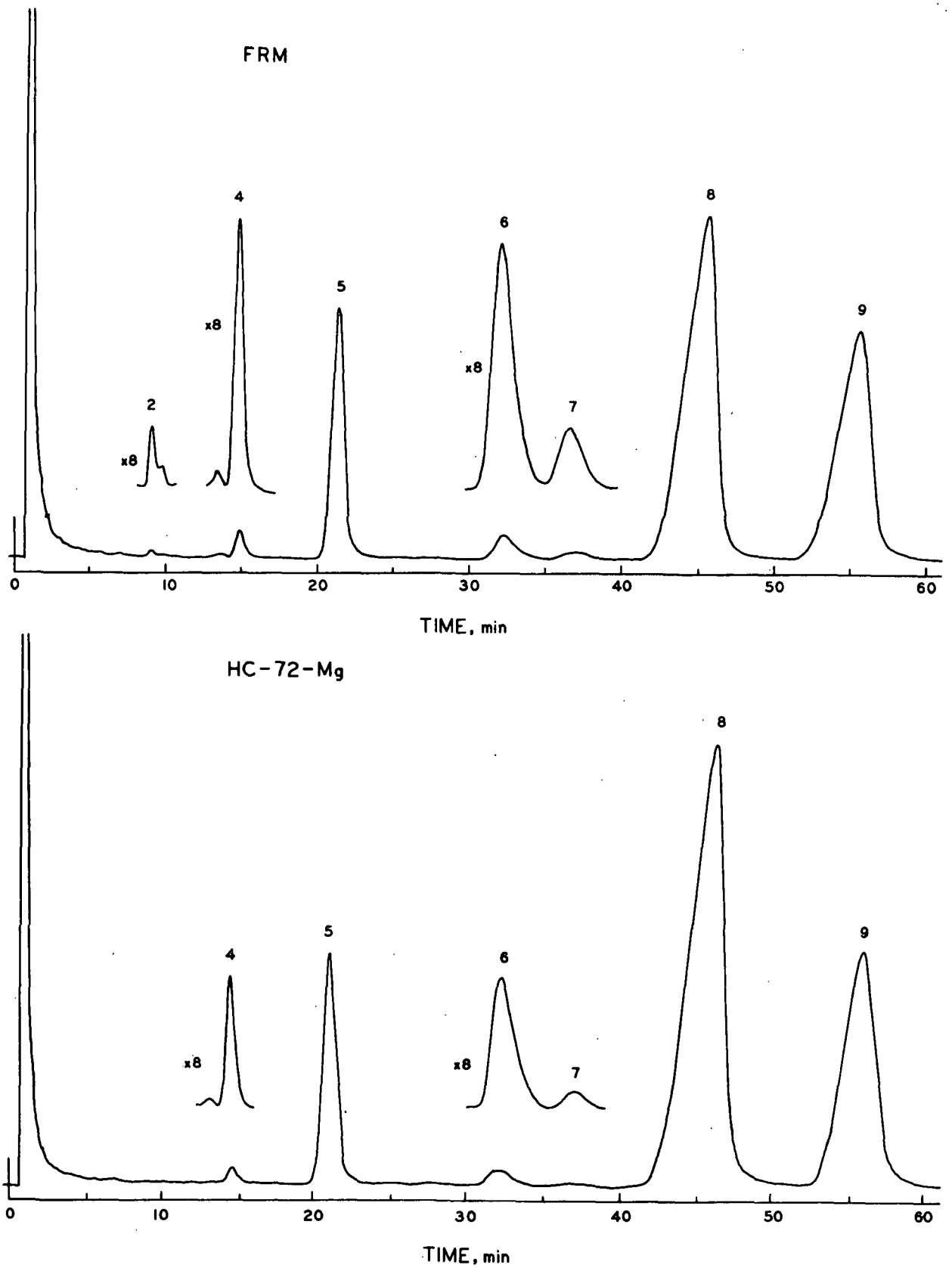


Figure 2. Neutral Sugar Analyses of Fiberized Red Maple (FRM) and a Corresponding 72% Yield Pulp: (2) Rhamnitol, (4) Arabinitol, (5) Xylitol, (6) Mannitol, (7) Galactitol, (8) Glucitol, and (9) myo-Inositol (Internal Standard)

TABLE I

GLYCAN ANALYSES
(wt.% of o.d. fiberized chips)

Material[a,b]	Yield[c]	Additive	Glucan	Xylan	Mannan	Arabinan	Galactan	Rhamnan	Total Glycan
FRM	--	--	46.2	14.9	2.2	0.9	0.6	0.2	65.0
(RM) (22)[d]			(46.6)	(17.3)	(3.5)	(0.5)	(0.6)	--	(68.5)
AT-FRM	90	--	43.2	13.0	1.8	0.7	0.3	0.1	59.1
HC-80	79	--	44.7	10.3	1.2	0.6	0.2	0.1	57.1
HC-72	72	--	43.4	9.0	1.1	0.5	0.3	0.0	54.3
HC-72-Mg	72	1% $MgCO_3$	43.5	9.7	1.3	0.4	0.1	0.0	55.0
HC-65	66	--	44.5	7.7	1.1	0.3	0.1	0.0	53.7
HC-65-Mg	65	1% $MgCO_3$	43.9	8.3	1.2	0.3	0.1	0.0	53.8
HC-65-KI	66	10% KI	44.3	10.7	1.2	0.1	0.1	0.0	56.4
LC-70	70	--	44.5	10.0	1.2	0.3	0.1	0.0	56.1
LC-66	66	--	44.6	9.6	1.1	0.3	0.1	0.0	55.7

[a] FRM, fiberized red maple chips; AT-FRM, sodium hydroxide treated FRM; HC and LC designate high and low consistency, respectively; Mg and KI indicate magnesium carbonate and potassium iodide additives, respectively.

[b] Project 3264 code numbers: HC-80, 12C; HC-72, 7C; HC-72-Mg, 22C; HC-65, 39C; HC-65-Mg, 42C and 65C; HC-65-KI, 69C; LC-70, 35/38C; and LC-66, 36.

[c] o.d. FRM basis.

[d] Extractive-free basis.

(HC-66, Table I). Thus, it appears from the limited number of pulps analyzed that the low consistency process may retain carbohydrates somewhat more selectively than the high consistency process.

Based on a limited number of analyses of oxygen-alkali spent liquors (9-10) available at that time, it was anticipated at the inception of this study (2) that hemicelluloses would be selectively removed relative to cellulose during pulping. This is clearly the case for the high consistency, sodium carbonate-oxygen process, as illustrated in Fig. 3. Except for a slight loss of glucan in the alkaline pretreatments, which may be related to some loss of glucomannan or low molecular weight cellulose, the glucan content remains essentially constant at ca. 44% of the original wood down to the 65% yield level. However, the hemicellulose content, reflected primarily in the xylan content, continually decreases throughout this yield range. Similarly, the loss of glucan in the low consistency process is very minor down to the 65% yield level, with the final glucan content of the pulp being the same as in the high consistency process. However, somewhat more xylan may be retained in the low consistency process (see Table I).

Compounds such as magnesium carbonate (23) and potassium iodide (24) have been added to oxygen-alkali processes primarily in an attempt to inhibit depolymerization of the wood polysaccharides, particularly cellulose. Whether these "inhibitors" can also decrease carbohydrate losses is also of interest. The data in Table I indicate that in the high consistency process, 1% magnesium carbonate (o.d. FRM basis) had no significant effects on the amount of carbohydrate retention at either the 72 or 65% yield level. Potassium iodide at the 10% level did increase the retention of carbohydrates, primarily xylan, but at a more practical level of addition the effect would be very small.

Figure 3. Carbohydrate Content versus Yield for FRM Pulps Prepared by the High Consistency Process

SPENT LIQUOR ANALYSES

The loss of carbohydrate from wood or pulp during alkaline processes is not necessarily due only to the peeling reaction in which the polysaccharides are degraded to acidic monomeric units. Polysaccharides with a low degree of polymerization, particularly if they possess acidic functional groups, can dissolve in an alkaline liquor without prior degradation. One potential method of estimating the molecular size of material in a spent liquor, and thus assessing the relative importance of peeling versus dissolution, is ultrafiltration in conjunction with sugar analyses.

Ultrafiltration or molecular filtration is a method for separating dissolved or colloidally suspended molecules on the basis of size by solvent flow through an anisotropic "skinned" membrane (25). Solutes, colloids, or particles having dimensions larger than the specified membrane "cut-off" remain with the retained solution, while materials smaller than the membrane pores pass through the membrane with solvent. Membranes are available in several different selective ranges, from very large to rather small macromolecules. The retentive abilities of the membranes are described by nominal limits; i.e., the membrane will hold back most, but not all molecules above a designated size. Although retention is primarily determined by the size and shape of the solute molecules, the membrane's retentive properties are normally described in terms of solute molecular weight. Thus, membranes are assigned a nominal molecular weight limit, which is determined by ability to retain specific reference molecules in their simple solutions.

Thus far, we have used Amicon UM-10 and UM-2 membranes for fractionating pulping spent liquors. The UM-10 and UM-2 membranes have nominal molecular weight

cut-off limits of 10,000 and 1,000, respectively, as calibrated with globular proteins (26).

The results of ultrafiltration analyses of spent liquors performed thus far are reported in Table II. The liquor solids retained by the UM-10 and UM-2 membranes are reported as a percentage of the total liquor solids and also as a percentage of the material lost from the pulp. However, the latter values are questionable because the weights of the retained solids have not been corrected for their ash contents, which must still be determined. Qualitatively, the ash contents of the retentates appear to be quite high.

Neutral sugar analyses of the UM-10 retentates are also reported in Table II.

The reproducibility of the fractionation of spent liquor solids by ultrafiltration appears to be fairly good. This is indicated by the results of duplicate analyses of the alkaline pretreatment spent liquor (AT-FRM, Table II) performed under similar conditions. However, the effect of drastic changes in the process variables such as volume of elution solvent, solvent flow rate, previous membrane usage, etc., on the fractionation has not been studied.

A substantial portion of the solids in all of the spent liquors were of sufficient molecular size to be retained on a UM-10 membrane; considerably less material was retained on the UM-2 membrane. Based on the retention limit of the UM-10 membrane, the degree of polymerization of retained polysaccharides, unassociated with lignin, would have to be greater than ca. 60. Since the polysaccharides in the spent liquor are essentially hemicelluloses, principally xylan, those retained on the UM-10 membrane have not been degraded extensively in being removed from the pulp. However, based on neutral sugar analyses, even with

TABLE II

SPENT LIQUOR ANALYSES

Liquor Source[a]	Stage	Retention, % of liquor solids UM-10	UM-2	Retention,[b] % of pulp loss UM-10	UM-2	UM-10 Neutral Glycan Analyses (wt.% of v.d. solids)[b,c] Total	Glucan	Xylan	Mannan	Galactan	Arabinan	Rhamnan
AT-FRM	--	37[d]	2	53[d]	3	24.8	1.6	14.9	1.0	3.5	1.9	1.9
		36[d]	4	53[d]	6	--	--	--	--	--	--	--
HC-80[e]	--	57	12	77	16	19.7	0.4	15.3	0.2	0.8	2.5	0.6
HC-72[f]	1st	59	10	34	6	16.2	0.2	13.0	0.1	0.6	1.9	0.4
	2nd	54	7	32	4	11.3	0.1	8.5	0.1	0.6	1.7	0.3
HC-72-Mg[f]	1st	46	3	33	4	20.3	0.2	15.8	0.4	0.8	2.3	0.8
	2nd	47	11	26	6	12.6	0.2	9.2	0.1	0.6	2.0	0.5

[a] See Table I for pulp descriptions.
[b] Weights of retained solids not corrected for ash contents.
[c] v.d., vacuum dried over phosphorus pentoxide.
[d] Includes material retained on the 0.45 micron filter also.
[e] One four-hour stage.
[f] Two four-hour stages.

allowances made for unanalyzed uronic acids, less than 25% of the UM-10 retentates from the oxygen-sodium carbonate liquors are carbohydrate. Based on the neutral sugar analyses in Tables I and II, ca. 35 and 45% of the carbohydrates lost in preparing HC-72 and HC-72-Mg, respectively, from AT-FRM are accounted for in the UM-10 retentates of the respective spent liquors. Similarly, only ca. 25% of the carbohydrates removed from FRM in the sodium hydroxide pretreatment are accounted for in the UM-10 retentate of the spent liquor. Since the quantity of UM-2 retentate is small, it appears that a significant portion of the polysaccharides removed during both pretreatment and pulping are degraded to very low molecular weight (<1000) species. In addition, magnesium carbonate in the pulping liquor does not significantly affect the result.

DEGREE OF POLYMERIZATION ANALYSES

Background

The major problem in investigating changes in the degree of polymerization of the wood polysaccharides is conversion of the polysaccharides, ideally without degradation, to derivatives suitable for analysis. Two basic approaches to the problem are available. First, direct nitration of the polysaccharides is presumably applicable to materials containing up to 23% lignin (27-28). Second, the lignin associated with the polysaccharides can be removed before the polysaccharides are derivatized. When the lignin is removed with minimal loss of polysaccharides, the product is called holocellulose.

For degree of polymerization (DP) analyses, we are assessing the feasibility of using the carbanilate derivatives of chlorine-ethanolamine and acid-chlorite holocelluloses of the pulps in conjunction with gel permeation (exclusion) chromatography (GPC). Valtasaari and Saarela (29) have reported that cellulose tricarbanilate (Fig. 4) can be used for determining the DP

distribution of cellulose by exclusion chromatography. In addition, E. L. Ashmawy, et al. (30) have used the carbanilate derivative in analyses of molecular weight distributions of cellulosic pulps containing up to 20% hemicellulose.

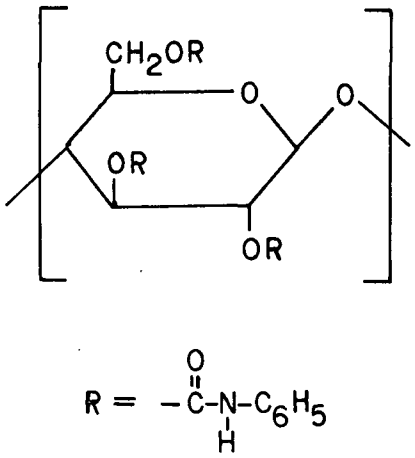


Figure 4. Monomer Unit of Cellulose Tricarbanilate

The carbanilate derivative is reported to be preferable to the frequently employed nitrate because the stability of the nitrate, both dry and in solution, is limited and there is risk of degradation of the polysaccharides during nitration (29-30). Also, complete substitution in nitration is difficult to achieve, thus complicating the interpretation of results (29). On the other hand, carbanilation presumably provides full substitution without degradation of the polysaccharide chain (29-30). From the analytical viewpoint, a very practical advantage of the carbanilate derivative is that it is ideally suited for use with a chromatography system employing an ultraviolet detector, since the derivative absorbs quite strongly at 235 nm (Fig. 5).

Analytical Method

Determination of the molecular weight or DP distribution of a polymer sample involves separation of the molecules according to size, and experimentally evaluating both the size and the relative proportions of molecules in the sample.

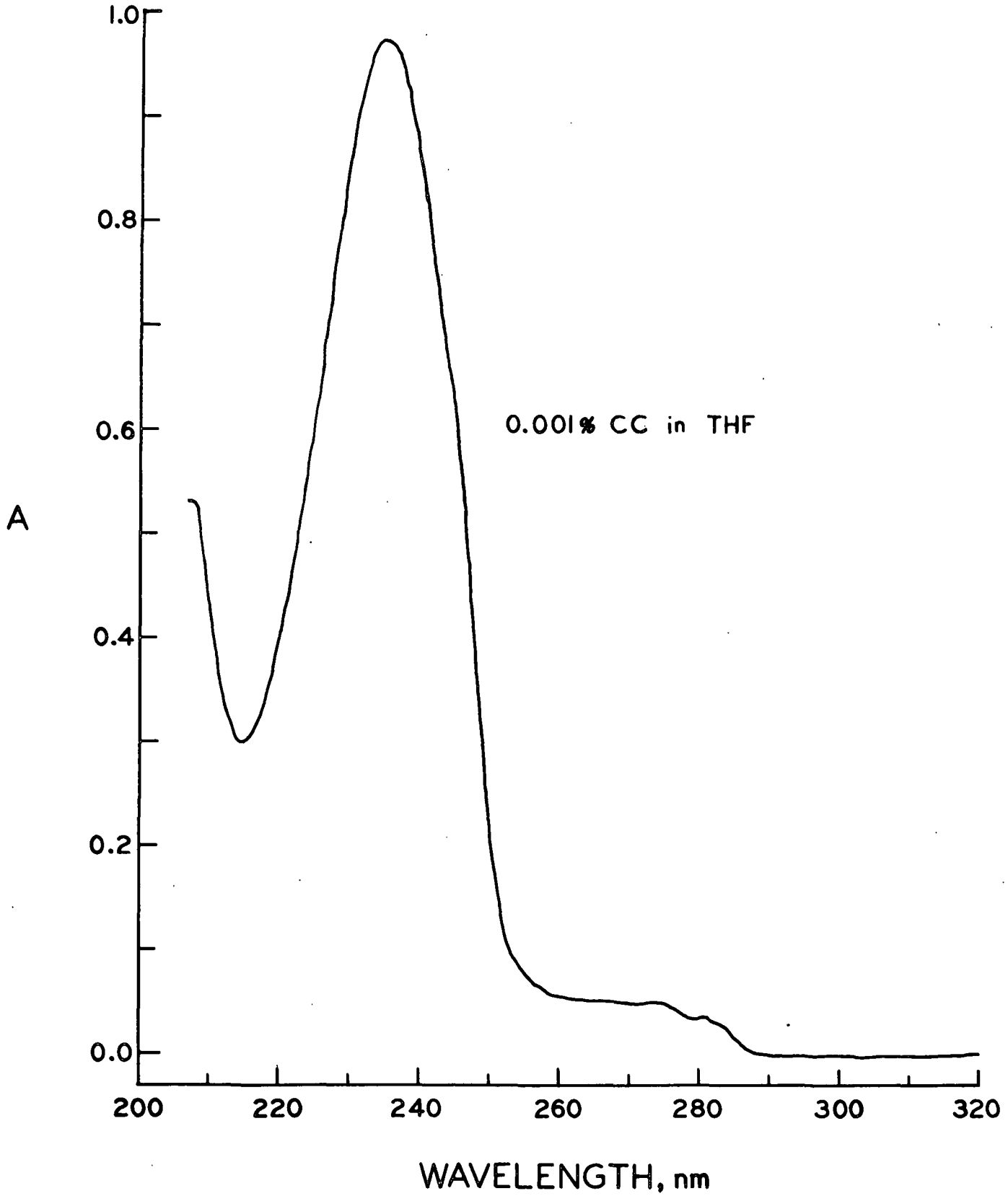


Figure 5. Ultraviolet Spectrum of Cellulose Tricarbanilate (CC) in Tetrahydrofuran (THF)

In GPC the separation of polymer molecules is achieved by eluting the sample solution through columns of porous molecules. The capacity of the polymer molecules to penetrate the pores of the column packing is inversely proportional to their size. Thus, the largest polymer molecules elute from the column system first, the smallest molecules last. Interpretation of the elution curve depends upon the calibration of the column system, which is the correlation between molecular size of the polymer molecules and their elution volumes. A direct calibration requires a series of well defined narrow molecular weight range fractions of the polymer of interest. In practice, the preparation and accurate characterization of such a set of samples is difficult. However, the universal calibration concept introduced by Benoit, et al. (31) makes it possible to evaluate GPC chromatograms of most polymers on the basis of a calibration of the column system with readily available polymer standards, such as polystyrene (see Fig. 11 and 12, Experimental).

The basic concept in the universal calibration (31) is that the elution velocity of the polymer molecule depends on its hydrodynamic volume. The product of the intrinsic viscosity and the polymer molecular weight, $[\eta]M$, is a direct measure of the hydrodynamic volume. Thus, under the same experimental conditions, all polymers having the same hydrodynamic volume, or $[\eta]M$, will be eluted with the same velocity, i.e., they will have the same elution volume.

The Mark-Houwink equation (Equation 1) relates the intrinsic viscosity of a polymer to its molecular weight. The constants K

$$[\eta] = KM^{\alpha} \qquad (1)$$

and α are characteristic for each polymer-solvent combination. Multiplying Equation 1 by the polymer molecular weight yields Equation 2.

$$[\eta]M = KM^{\alpha+1} \qquad (2)$$

Thus, GPC chromatograms obtained for polymer 1 can be analyzed on the basis of a column calibration made with polymer 2 through Equation 3.

$$K_1 M_1^{(\alpha_1+1)} = K_2 M_2^{(\alpha_2+1)} \qquad (3).$$

On the basis of Equation 3, a calibration curve (Fig. 6) relating the molecular weight of the polysaccharide percarbanilates to their elution volume (V_i), relative to the elution volume (V_s) of a reference compound, was constructed from the polystyrene calibration data (Fig. 12, Experimental). The values used for K and α were those reported for tetrahydrofuran solutions by Valtasaari and Saarela (29); 1.179×10^{-2} ml/g and 0.74, respectively, for polystyrene and 2.01×10^{-3} mg/g and 0.92, respectively, for cellulose tricarbanilate. El Ashmawy and coworkers (30) have reported similar K and α values for the percarbanilate of an 80% alpha-cellulose pulp; 2.51×10^{-3} ml/g and 0.89, respectively.

A GPC chromatogram of cellulose tricarbanilate prepared from an ICCA-1 pulp (32) is shown in Fig. 7. To determine the number-average ($\overline{M}_n$) and weight-average ($\overline{M}_w$) molecular weights from chromatograms, the ordinate height (h_i) was determined at 2-ml increments of the relative elution volume ($V_s - V_i$) over the entire elution curve. The molecular weights (M_i), corresponding to the $V_s - V_i$ values, were obtained from the tabular data used to construct Fig. 6. The number average molecular weight of the polysaccharide sample was calculated according to Equation 4; the weight average molecular weight according to Equation 5 (30).

$$\overline{M}_n = \Sigma h_i / \Sigma (h_i / M_i) \qquad (4)$$

$$\overline{M}_w = \Sigma h_i M_i / \Sigma h_i \qquad (5)$$

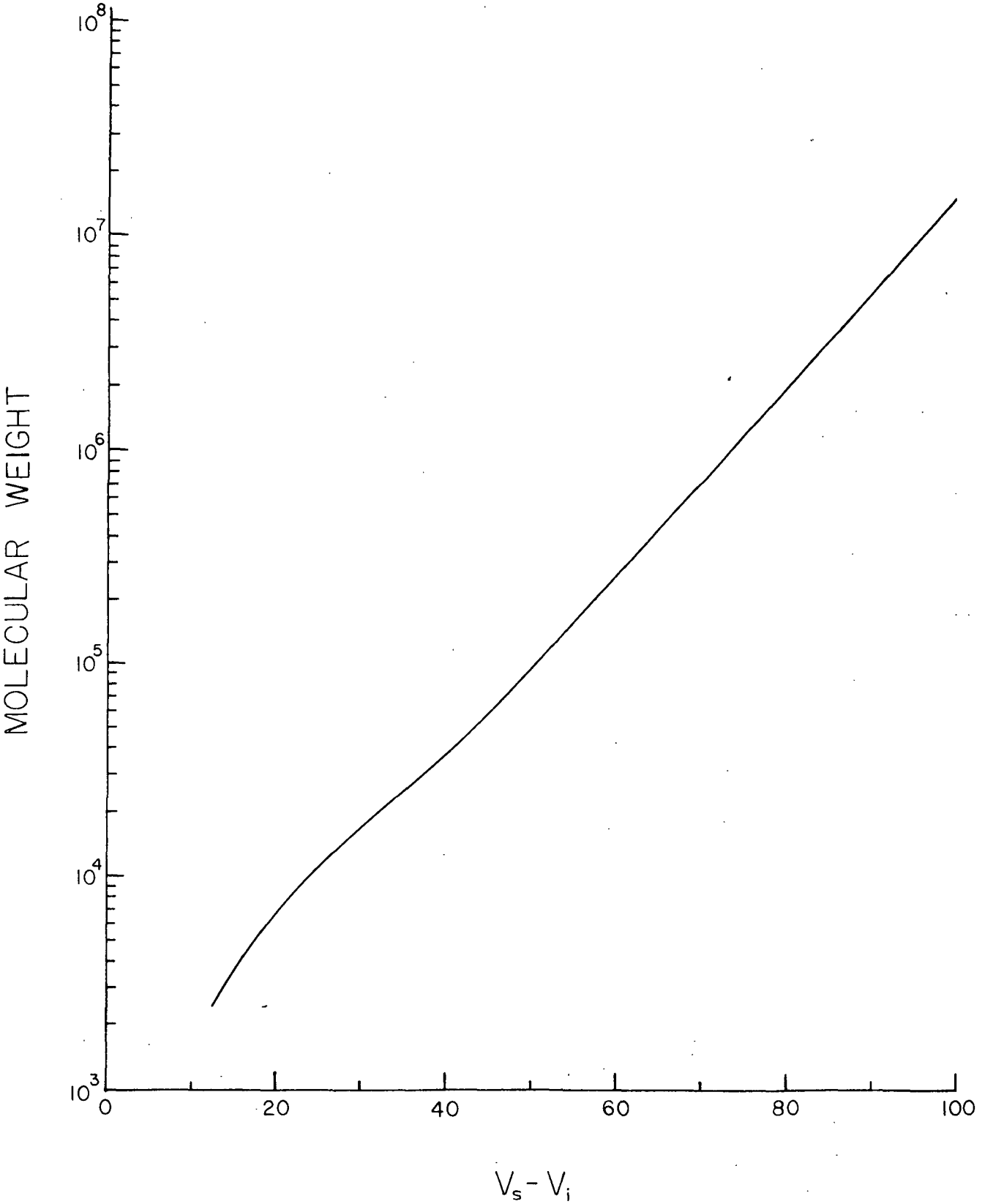


Figure 6. Cellulose Tricarbanilate Molecular Weight versus Relative Elution Volume ($V_s - V_i$)

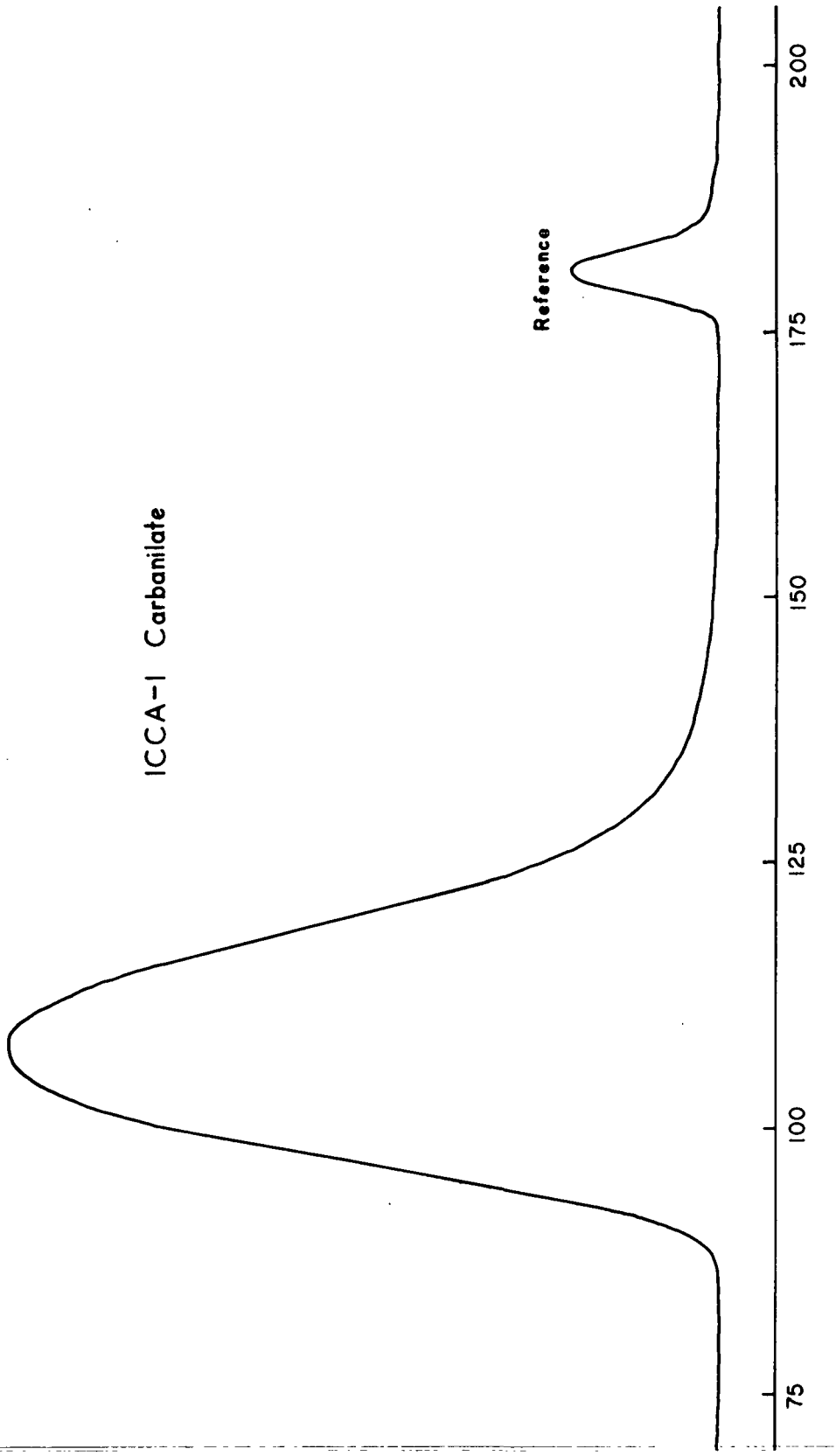


Figure 7. Gel Permeation Chromatogram of Cellulose Tricarbanilate on Styragel Columns
Eluted with Tetrahydrofuran

Apparent number-average DP ($\overline{DP}_n$) and weight-average DP ($\overline{DP}_w$) values were calculated by dividing the respective molecular weight values by the monomer equivalent weight of cellulose tricarbanilate, 519.

Polysaccharide Analyses

Initial attempts to apply the GPC method to polysaccharide analyses were directed toward analysis of a cellulose tricarbanilate prepared from an ICCA-1 pulp (Fig. 7). The results were encouraging in that a $\overline{DP}_w$ of 2350 was obtained. This value compares favorably with viscosity DP values determined for the ICCA-1 pulp (32).

Subsequent analyses of percarbanilates of holocelluloses from fibrized red maple chips (FRM) and a 72%-yield oxygen-sodium carbonate pulp (HC-72) are shown in Fig. 8. Qualitative differences in the chromatograms are immediately obvious. For example, the percarbanilate of the FRM holocellulose exhibits two maxima which are indicative of the cellulose and hemicellulose constituents. The contribution of the hemicelluloses in the HC-72 holocellulose is reflected only in the skewness of the elution curve. In addition, the overall values of $V_s - V_i$ for the HC-72 holocellulose are lower than those for the FRM holocellulose. This is indicative of some depolymerization of the polysaccharides occurring during the oxygen-sodium carbonate pulping process.

However, from a quantitative viewpoint problems were encountered with the analytical procedure. Since difficulties, such as insoluble gel formation and low yields, were encountered in the preparations of the percarbanilates of the FRM and HC-72 holocelluloses, various reaction conditions were explored in an attempt to obtain more satisfactory derivatization. The $\overline{DP}_w$ values of holocellulose percarbanilates prepared using various reaction conditions are reported in Table III. The results indicate that degradation of the polysaccharide can occur during

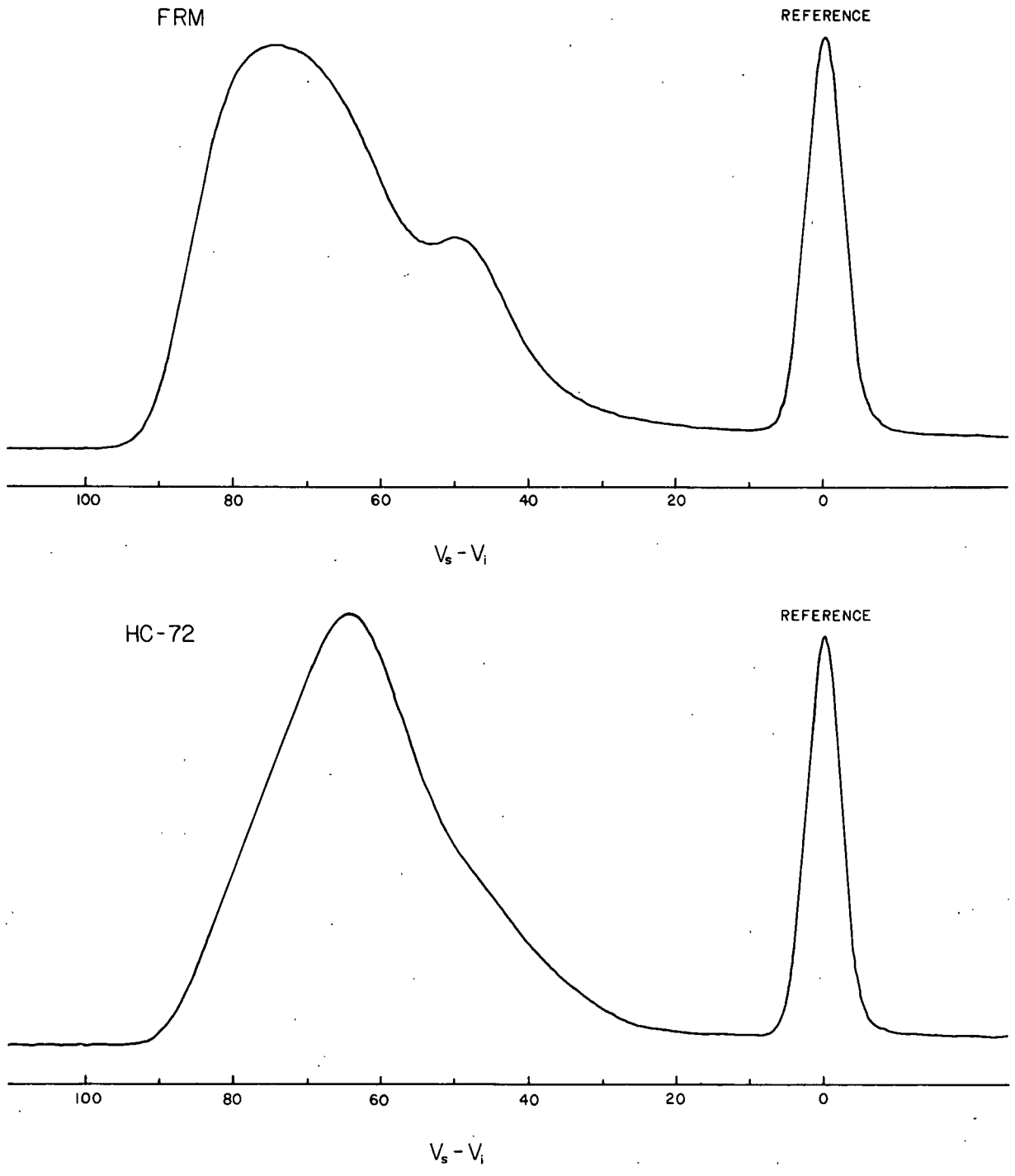


Figure 8. GPC Analyses of Percarbanilates of Holocelluloses from Fiberized Red Maple Chips (FRM) and a 72%-Yield Oxygen-Sodium Carbonate Pulp (HC-72) from FRM

carbanilation. However, the results were inconsistent. The difference in $\overline{DP}_w$ for FRM holocellulose after two days at 110°C and reflux temperature conditions was quite drastic; the same conditions for HC-72 holocellulose yielded carbanilates with essentially the same $\overline{DP}_w$.

TABLE III

EFFECTS OF DERIVATIZATION CONDITIONS ON THE $\overline{DP}_w$ OF HOLOCELLULOSE PERCARBANILATES[a]

Holocellulose	Temperature	Time, days	Carbanilate $\overline{DP}_w$
FRM	Reflux	1	2250
"	"	2	1480
"	"	4	1140
"	110°C	2	2213
"	80°C	2	1982
HC-72	Reflux	2	1396
"	110°C	2	1423
"	80°C	2	1676

[a]Pyridine solvent.

From the standpoint of attaining a clear, light yellow solution indicative of complete reaction (29), carbanilation under reflux conditions was the most desirable. Thus, it was of interest to ascertain whether degradation of the polysaccharides, under reflux conditions, could be minimized through use of an appropriate reaction time. Pyridine solutions of purified ICCA-1 percarbanilate and phenyl isocyanate, were refluxed for varying time periods, after which the carbanilate was isolated and analyzed by GPC. The results of the experiment are shown in Fig. 9. The $\overline{DP}_w$ of the carbanilate decreased drastically in the first 12 hours and then continued to decrease more slowly over the time span studied. Based on the severe degradation observed at reflux conditions, it is questionable whether statements that cellulose can be carbanilated without degradation (29-30), albeit at somewhat milder conditions, are accurate. However, the question of degradation at the milder conditions will be examined.

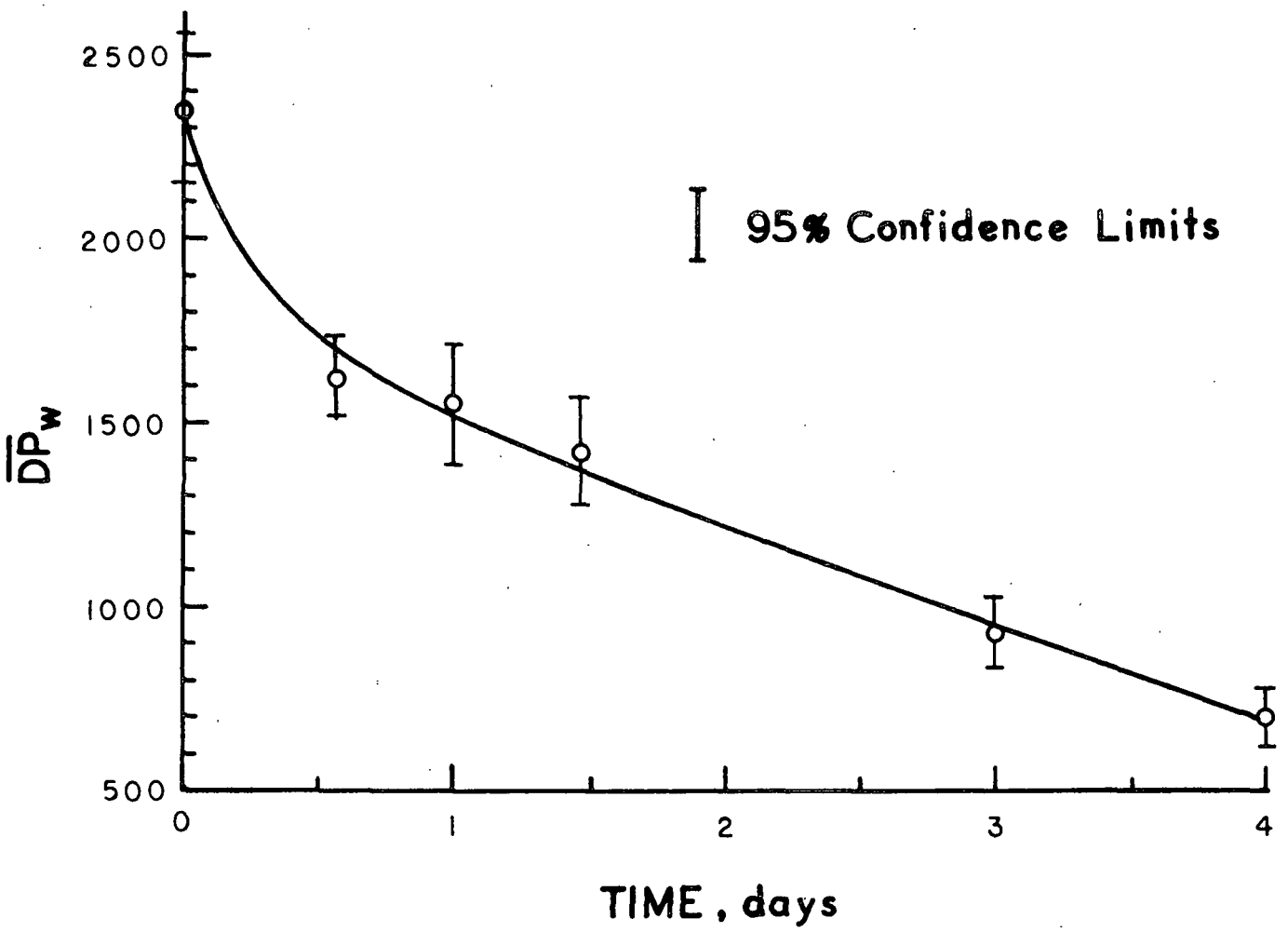


Figure 9. Degradation of Cellulose Tricarbanilate at Reflux Carbanilation Conditions

CONCLUSIONS

In both high and low consistency pulping of red maple with oxygen-sodium carbonate and oxygen-sodium carbonate-sodium bicarbonate, respectively, hemicelluloses are selectively removed relative to cellulose. The loss of cellulose is minimal down to the 65% yield level. In both pulping processes lignin is selectively removed relative to the carbohydrates, but the degree of selectivity is not very great. The degree of selectivity appears to be somewhat greater in the low-consistency process.

Magnesium carbonate at 1% loading (o.d. wood basis) does not affect carbohydrate retention in the high consistency pulping. Potassium iodide at 10% loading did increase carbohydrate retention, but at a more practical level of addition the effect would be very small.

As indicated by spent liquor analyses, a major portion of the carbohydrates removed from the pulp in the high consistency pulping process is degraded to low molecular weight (<1000) species. Magnesium carbonate does not have an appreciable effect on the degradation.

Gel permeation chromatography can be used for analysis of polysaccharide molecular weights, but degradation during derivatization is a problem which must be circumvented or minimized.

FUTURE WORK

Analyses will be initiated on additional red maple pulps prepared by the high consistency process and which reflect the effect of varying the reaction temperature and oxygen pressure. Low consistency red maple pulps prepared at a higher temperature and also with potassium iodide as an inhibitor will also be analyzed.

Work on determining whether carbanilation of the wood polysaccharides can be used in determining their molecular weight distribution will be continued. If carbanilation is shown to be inappropriate, other methods of derivatizing the polysaccharides for analysis will be explored.

Analyses of spent liquors from the preparation of red maple pulps will be continued. Of particular interest are spent liquors from the low consistency process and spent liquors from reactions using potassium iodide as an inhibitor.

Currently, attempts are being made to develop a method for analysis of the carboxylic acids in the oxygen-alkali pulps. The attempts are based on similar work by Johansson and Samuelson (33).

Analyses will be initiated on oxygen-alkali pulps from loblolly pine as the pulps become available.

EXPERIMENTAL

PULP AND SPENT LIQUOR SAMPLES

Pulps and spent liquors used in this project were generated as an integral part of a concurrent pulping study (Project 3264) under the direction of G. A. Nicholls (1). The pulps and spent liquors were stored in a cold room at 5°C until used. The pulps, as provided, had ovendry contents of ca. 25 to 30%. Portions of the pulp samples were subsequently air dried in a forced-air oven and then Wiley milled using a No. 40 screen.

ANALYTICAL METHODS

Melting points were determined on a Thomas Hoover capillary apparatus which was calibrated against known compounds. Polarimetric measurements were made on a Perkin-Elmer 141 MC polarimeter. Ultraviolet spectra were determined on a Cary 15 recording spectrophotometer. Infrared spectra were determined on a Perkin-Elmer 700 instrument.

Thin layer chromatography (TLC) was performed on plates coated with silica gel G utilizing methanolic sulfuric acid (5:1, wt.) spray with charring for components detection.

Gas chromatographic (GLC) analyses were performed on a Varian Aerograph 2740 instrument equipped with a flame ionization detector and a Varian 25 recorder with a Disk integrator. Analyses were performed with: (A) 3% SP-2340 on 100-200 mesh Supelcoport (Supelco, Inc.) column (10 ft. x 0.125 inch o.d. stainless steel); column, 205°C; N_2, 30 ml min^{-1}; injector, 250°C; detector, 260°C; and on-column injection and (B) 3% ECNSS-M on 100-120 mesh Gas Chrom Q (Applied Science Laboratories, Inc.) column (7 ft. x 0.125 inch o.d. stainless steel); column, 190°C; N_2, 30 ml

min^{-1}; injector, 250°C; detector, 260°C; and on-column injection. Retention times (T_r) of various alditol peracetates and myo-inositol peracetate are given in Table IV.

TABLE IV

POLYOL PERACETATE GLC RETENTION TIMES[a,b]

Polyol Peracetate	T_r, min	
	SP-2340 Column	ECNSS-M Column
L-rhamnitol	9.5	7.5
L-arabinitol	15.0	12.5
Xylitol	21.6	17.8
D-mannitol	32.4	32.0
Galactitol	37.3	36.7
G-glucitol	46.5	45.8
myo-Inositol	55.6	57.0

[a]Analysis conditions are described in the text.
[b]Retention times listed are for new columns.

Liquid chromatographic (LC) analyses were performed on a Varian 8500 chromatograph, utilizing a Perkin-Elmer LC-55 spectrophotometer equipped with a flow cell as the detector. Four styragel columns (Waters Associates) having permeability ranges of 10^6, 10^5, 10^4, and 10^3 A were linked in series and adapted to fit the Varian chromatograph. Analyses were performed at ambient temperature using tetrahydrofuran as the elution solvent at a flow rate of 2.0 ml min^{-1}. Detector wavelengths of 225 and 235 nm were used for analyzing polystyrene and polysaccharide percarbanilates, respectively. Tetrahydrofuran was purified for LC use by refluxing it with lithium aluminum hydride and then fractionally distilling it through a 40-cm column packed with Raschig rings (34).

COMPOUND SYNTHESES

Alditol Peracetates

L-Arabinitol (Aldrich Chemical Company), erythritol (Pfanstiehl Laboratories), D-glucitol, sorbitol; (Matheson, Coleman, and Bell), D-mannitol (Pfanstiehl Laboratories), ribitol (Pfanstiehl Laboratories), and xylitol (Aldrich Chemical Company) were acetylated with acetic anhydride in pyridine (35). The acetylations were monitored by TLC using chloroform-ethyl acetate (4:1, vol) as the developing solvents. Ribitol pentaacetate was purified by column chromatography on silica gel (Mallinckrodt SilicAR CC-7, 100-200 mesh) using chloroform-ethyl acetate (6:1, vol) as the eluent, and isolated as an oil. The other alditol peracetates were purified by crystallization from absolute ethanol. The purity of the alditol peracetates was checked by GLC using conditions A. The physical properties of the alditol peracetates are given in Table V.

TABLE V

PHYSICAL PROPERTIES OF ACETYLATED REFERENCE COMPOUNDS

Peracetate	m.p., °C[a]	$[\alpha]_D$ (°), $CHCl_3$[a]
Erythritol	85-86 (85-86) (36)	0.0
L-arabinitol	74-75 (76) (37)	-37.2 (-36) (37)
Ribitol	Oil (51) (38)	0.0
Xylitol	62-63 (62-63) (39)	0.0
Galactitol	170-171 (168-169) (40)	0.0
G-glucitol	98-99 (99) (40)	+10.0 (+10.0) (40)
D-mannitol	124-125 (126) (40)	+25.8 (+25.0) (40)
L-rhamnitol	Oil	-33.9
myo-Inositol	216-217 (214-215) (41)	0.0

[a]Figures in parentheses are the values reported in the indicated literature references.

L-rhamnitol, obtained by reduction of L-rhamnose (Pfanstiehl Laboratories) with sodium borohydride (42), was acetylated with acetic anhydride in pyridine (35). The L-rhamnitol pentaacetate was purified by decolorization with carbon and column chromatography on silica gel (SilicAR CC-7), 100-200 mesh using chloroform-ethyl acetate (8:1, vol) as the eluent. The L-rhamnitol pentaacetate was isolated as a very viscous oil (see Table V); its purity was assessed by TLC and GLC as described above.

Galactitol (dulcitol, Aldrich Chemical Company) was acetylated with acetic anhydride using sulfuric acid as a catalyst (20,41). The galactitol hexaacetate was purified by crystallization from absolute ethanol; its physical properties are given in Table V.

myo-Inositol Hexaacetate — myo-Inositol (Calbiochem) was acetylated with acetic anhydride using sulfuric acid as a catalyst and isolated by precipitation from boiling water (41). The physical properties of the myo-inositol hexaacetate are given in Table V.

Cellulose Tricarbanilate — Cellulose tricarbanilate was prepared from an ICCA-1 pulp (32) by reaction of the pulp with phenyl isocyanate in pyridine, basically as outlined by Valtasaari and Saarela (29). The amount of phenyl isocyanate used was increased to 35 times the stoichiometric quantity. In addition, the precipitated polymer was subjected to a final wash with water and then freeze-dried at each isolation stage.

N-Phenyl Cyclohexyl Carbomate — Anhydrous cyclohexol (10.1 ml) (43) and phenyl isocyanate (8.1 ml) were mixed together. The resultant reaction generated considerable heat and, upon cooling, a crystalline mass was obtained. The crystals

were recrystallized from petroleum ether (b.p. 60-110°C) to yield N-phenyl cyclohexyl carbomate, m.p. 81-82°C. Literature: m.p. 82°C (44).

HOLOCELLULOSE PREPARATION

Chlorination-Extraction Method — The procedure is a slight modification of a procedure reported by Holmes and Kurth (45). The apparatus used is illustrated in Fig. 10.

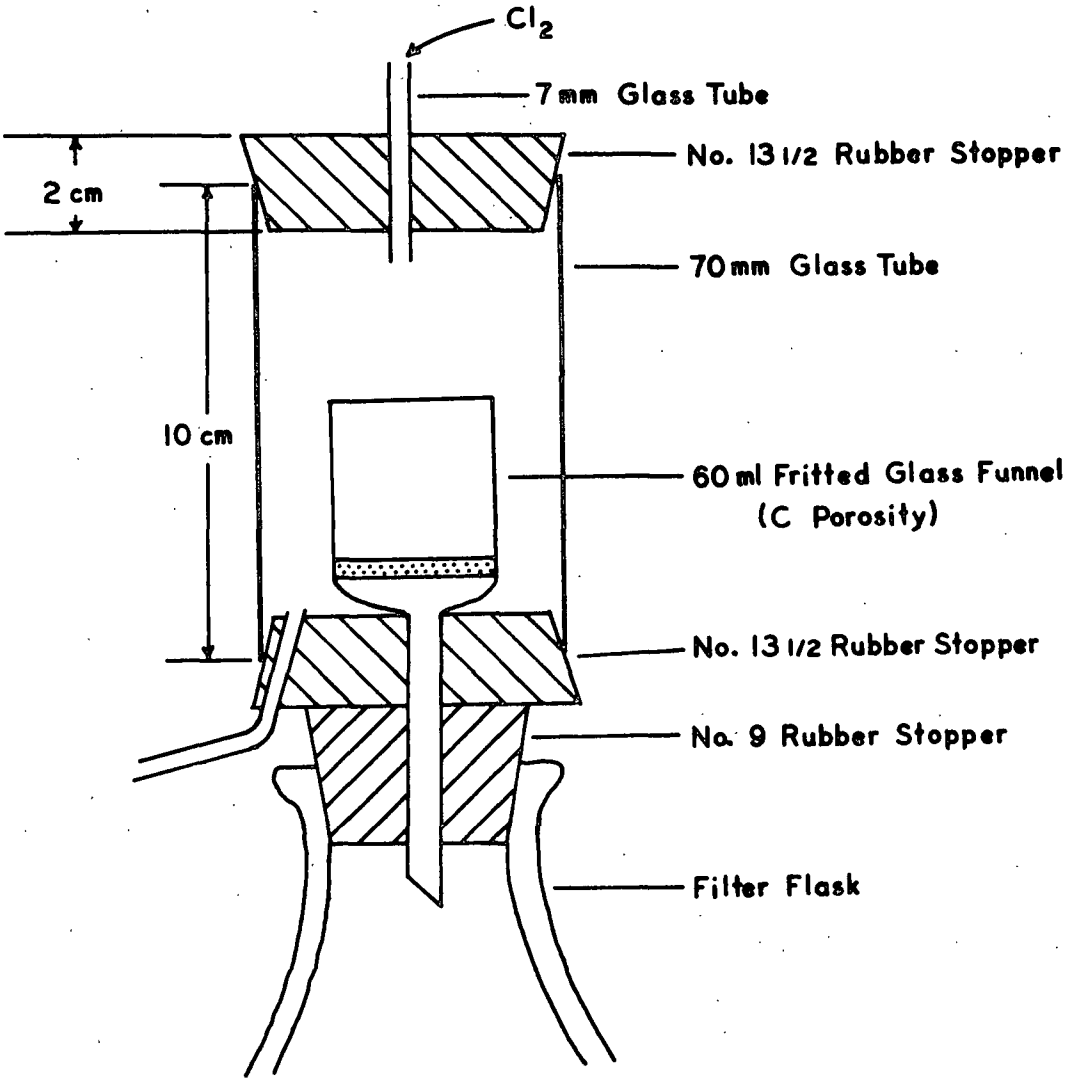


Figure 10. Apparatus for Preparing Holocellulose

A sample (ca. 2 g o.d.) of never-dried pulp was slurried with 0.01M $CaCl_2$ and filtered into the fritted glass funnel. The apparatus was assembled as shown in Fig. 10, with ice and water surrounding the funnel containing the moist pulp. Using a slight vacuum in the filter flask, chlorine gas was passed through the pulp for 2.5 minutes. The sample was then covered with 1,4-dioxane at room temperature, the mixture was stirred, and the dioxane was removed by vacuum. After the ice water was drained from the apparatus, the pulp was treated with two successive portions of 5% (vol) monoethanolamine in dioxane at 50°C. Each time the dioxane and base were allowed to stand with the pulp for 2 minutes before being removed by vacuum. The sample was then washed twice with dioxane at room temperature and twice with cold aqueous 0.01M $CaCl_2$.

The entire procedure, beginning with chlorination, was repeated until the sample appeared white after chlorination, or when very little color change occurred upon addition of the basic dioxane solution.

The resulting holocellulose was washed with dioxane until neutral and finally with 0.01M $CaCl_2$. It was then slurried with ca. 50 ml of distilled water, and the mixture was frozen and freeze-dried. Freeze-drying gives a material which is more easily dispersed for subsequent derivatization.

Caution! During the second or third (final) chlorination of the more highly oxidized pulps, a flash fire would frequently occur in the gas phase of the vacuum flask. A considerable amount of soot would form in the flask, as well as the vacuum tubing.

Acid-Chlorite Method — A stock chlorite solution was prepared by mixing water (99 g), sodium chlorite (5.0 g), and glacial acetic acid (1.0 g) together.

Chlorite solution (20 ml) was added to a sample (ca. 2 g o.d.) of never-dried pulp in a large test tube. The tube was tightly stoppered and placed in the dark for 24 hours. The resultant holocellulose was filtered on a sintered glass funnel, washed with 5 liters of distilled water, slurried with 50 ml of distilled water, frozen, and freeze-dried.

NEUTRAL SUGAR ANALYSIS

The air-dried, Wiley-milled pulp, or other material for analysis, was dried in vacuo overnight over phosphorus pentoxide. The sample was hydrolyzed with acid and the monomeric sugars were converted to the corresponding alditols by reduction with sodium borohydride (20). After acetylation with acetic anhydride using sulfuric acid as a catalyst, the alditols were analyzed by GLC using Conditions A. myo-Inositol was used as an internal standard.

The individual glycan contents of the samples were calculated according to Equation 6.

$$\% \text{ Glycan} = 100 \, (A_g/A_i) \, (W_i/W_s) \, (F_c/F_r) \qquad (6)$$

where A_g = chromatographic area of the component peak

A_i = chromatographic area of the internal standard peak

W_i = weight of the internal standard

W_s = oven-dry weight of the sample

F_c = factor to convert glycose to glycan (0.88, pentose; 0.90, hexose; and 0.89, monodeoxy-hexose)

F_r = hydrolysis survival-response factor.

The requisite hydrolysis survival-response factors (F_r) for the analytical procedure were determined by subjecting six known mixtures of the required monosaccharides to the total procedure. The survival-response factors were calculated according to Equation 7 and are reported in Table VI.

$$F_r = (A_g/A_i)\ (W_i/W_g) \qquad (7)$$

where A_g, A_i, and W_i are as defined previously and

W_g = weight of the respective glycose in the initial mixture.

TABLE VI

HYDROLYSIS SURVIVAL-RESPONSE FACTORS[a]

Glycose	F_r[b]
L-arabinose	0.922 (0.015)
D-galactose	0.794 (0.029)
D-glucose	0.932 (0.025)
D-mannose	0.869 (0.019)
L-rhamnose	0.724 (0.029)
D-xylose	0.843 (0.039)

[a] Determined using GLC Conditions A.
[b] Figures in parentheses are the 95% confidence limits.

SPENT LIQUOR FRACTIONATION

Sodium Hydroxide Pretreatment Liquor — The solids content and density of the alkaline pretreatment liquor were determined. The liquor was filtered through 0.45 micron Metrical membranes using Gelman pressure filtration units, with up to 100 psig nitrogen pressure. The solids content of the filtrate was determined and the pH of the solution was adjusted to ca. 8.5 with 30% acetic acid. The filtration residue was recovered from the membranes and freeze-dried.

A known volume of filtrate (ca. 300 ml) was subjected to ultrafiltration with an Amicon 402 stirred cell (Amicon Corporation) using a UM-10 membrane (26). Approximately 3.5 liters of distilled water was used in the filtration. The solution of retained solute was concentrated in vacuo until material began to precipitate and was then freeze-dried. The effluent was concentrated in vacuo to ca. 300 ml and subjected to fractionation on a UM-2 membrane in a similar fashion. Both the solution of retained solute and the effluent were concentrated in vacuo and then freeze-dried.

Pulping Spent Liquors — Spent liquors obtained from the preparation of comparable pulps were combined and filtered to eliminate large particulate matter. The pH, solids content, and the density of the composite liquor were determined. A known volume of the composite liquor was concentrated in vacuo to 200-300 ml and the volume, pH, and the solids content of the liquor were determined. After addition of formaldehyde (0.5%, wt.), the liquor was subjected to ultrafiltration with UM-10 and UM-2 membranes, as described above. In each fractionation, the solution of retained solute was concentrated in vacuo to 50-100 ml, frozen, and freeze-dried. The final effluent from the UM-2 fractionation was treated similarly.

DEGREE OF POLYMERIZATION ANALYSIS

Calibration of Styragel Columns — The Styragel columns used in liquid-chromatographic analyses of polysaccharide molecular weights were calibrated with eleven "monodisperse" polystyrene standards, with molecular weights ranging from 2.1×10^3 to 3.56×10^6. Tetrahydrofuran solutions of the polystyrene standard (0.5%) and the reference, N-phenyl cyclohexyl carbomate (5%), were injected separately onto the columns and then analyzed simultaneously to obtain a series of chromatograms as illustrated by the composite chromatogram in Fig. 11. The elution volumes of N-phenyl cyclohexyl carbomate (V_s) and the polystyrene standard (V_i) were taken

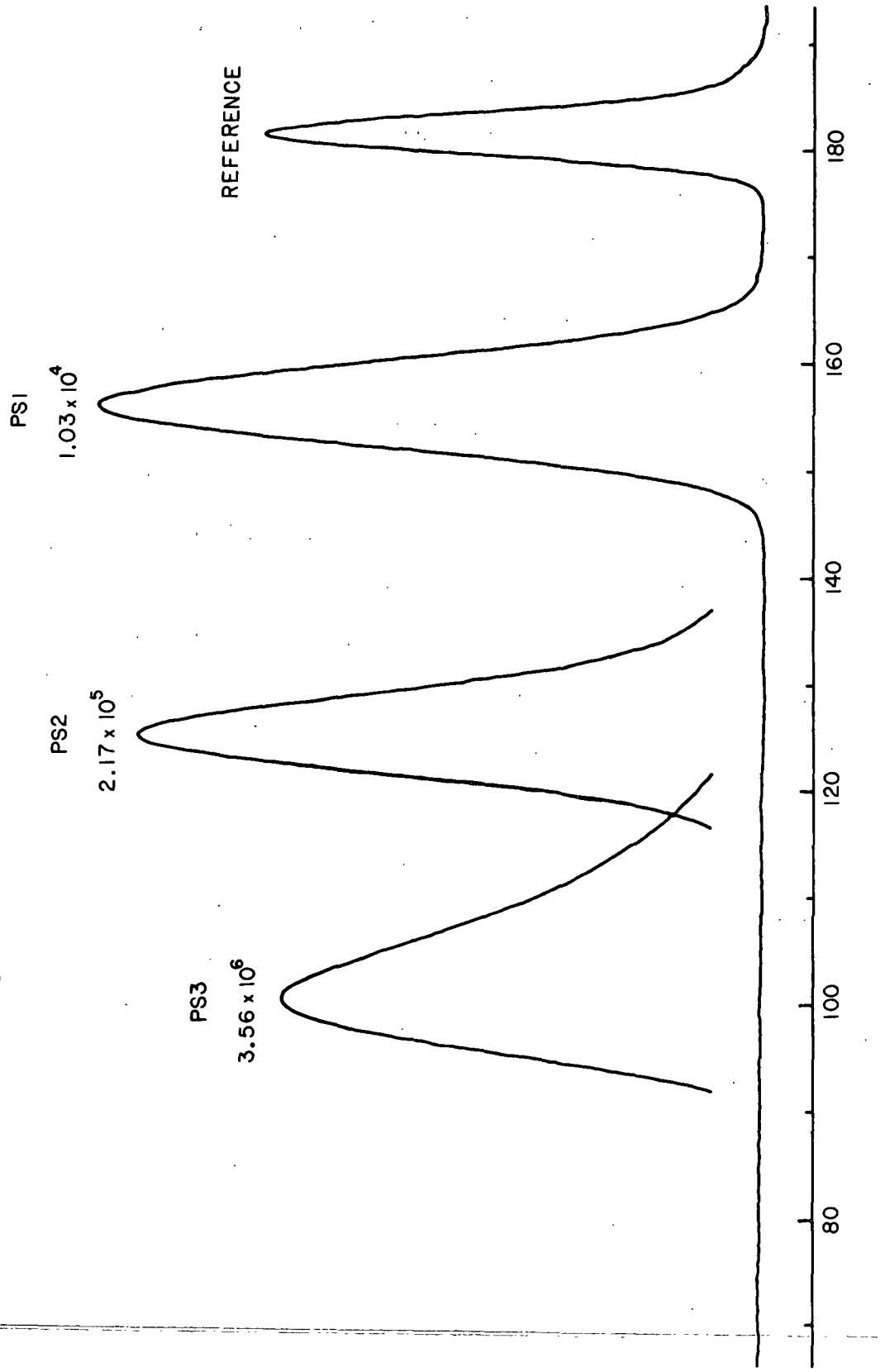


Figure 11. Composite Gel Permeation Chromatogram of Polystyrene Standards on Styragel Columns Eluted with Tetrahydrofuran

to be the apices of their respective elution curves calculated to the nearest milliliter. A calibration curve (Fig. 12) relating polystyrene molecular weight to the quantity $V_s - V_i$ was then constructed from the data. The elution volume of N-phenyl cyclohexyl carbomate (V_s) was used as the reference point in the chromatograms to obtain better reproducibility.

Holocellulose Derivatization — The freeze-dried holocellulose was dried overnight *in vacuo* over phosphorus pentoxide. Anhydrous pyridine (200 ml) (34) was added to the dried holocellulose in a reflux apparatus. Pyridine (*ca.* 30 ml) was distilled from the mixture to dry the system, phenyl isocyanate (21 ml) was added to the mixture, and the reaction was protected from atmospheric moisture with a drying tube. The mixture was brought to desired temperature and allowed to react for the desired length of time. When the reaction temperature was less than boiling, the mixture was stirred magnetically.

The reaction mixture was cooled to *ca.* 60°C and methanol (21 ml) was added to the mixture to react with the excess phenyl isocyanate. The mixture was diluted with dioxane (15-25 ml) to reduce the viscosity, centrifuged, and filtered through two glass filter pads (Reeve Angel 934AH). The filtrate was poured in a very fine stream into a stirred solution of methanol (1500 ml) and acetic acid (10 ml). The precipitated polymer was isolated, washed with a solution of water (1000 ml) and acetic acid (20 ml), washed with water (1500 ml), and freeze-dried.

Chromatographic Analysis — Liquid-chromatographic analysis of tetrahydrofuran solutions (0.5%) of the polysaccharide percarbanilates were made using the internal reference as described previously. A chromatogram is illustrated in Fig. 13.

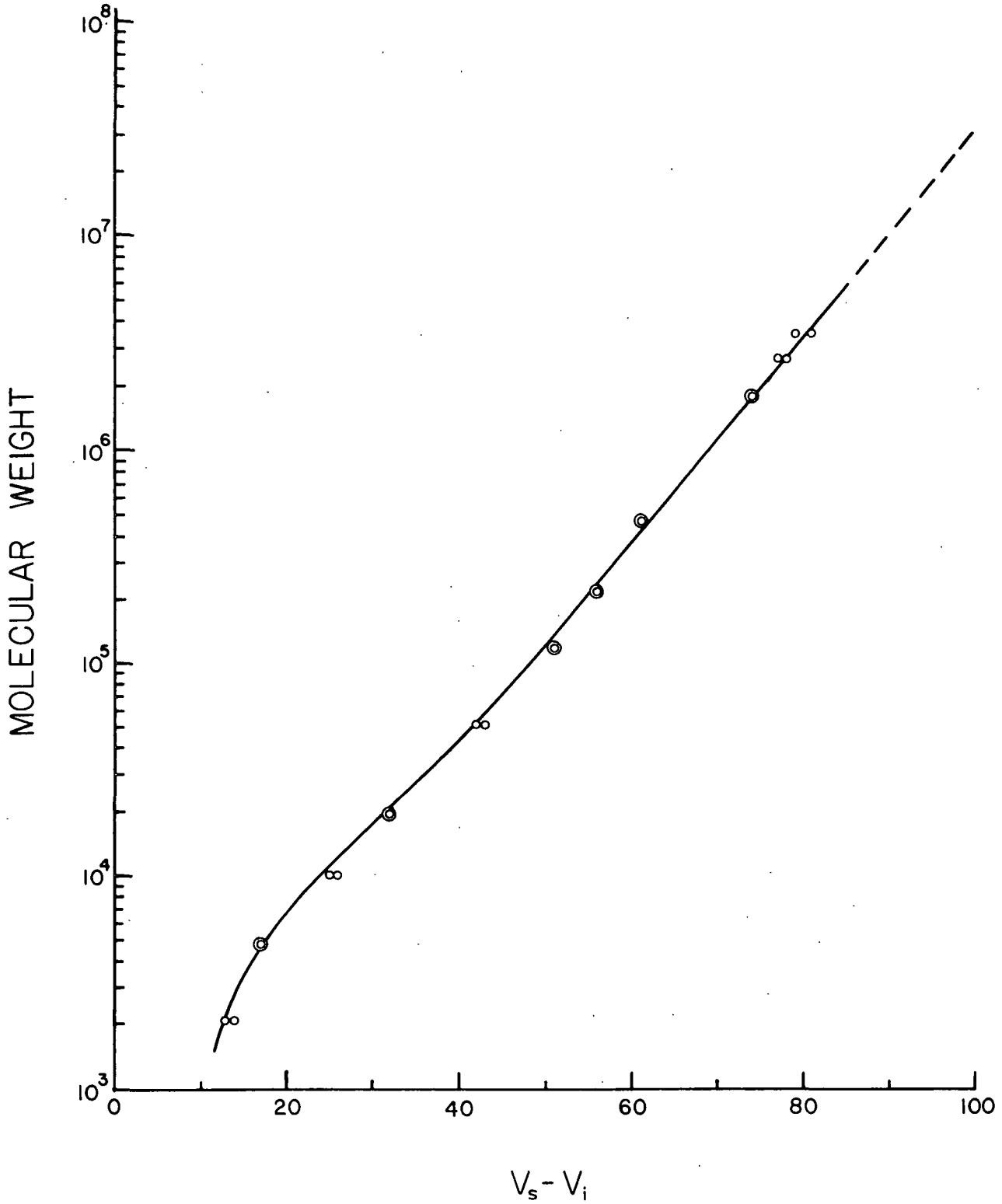


Figure 12. Calibration Curve for Polystyrene Standards on Styragel Columns

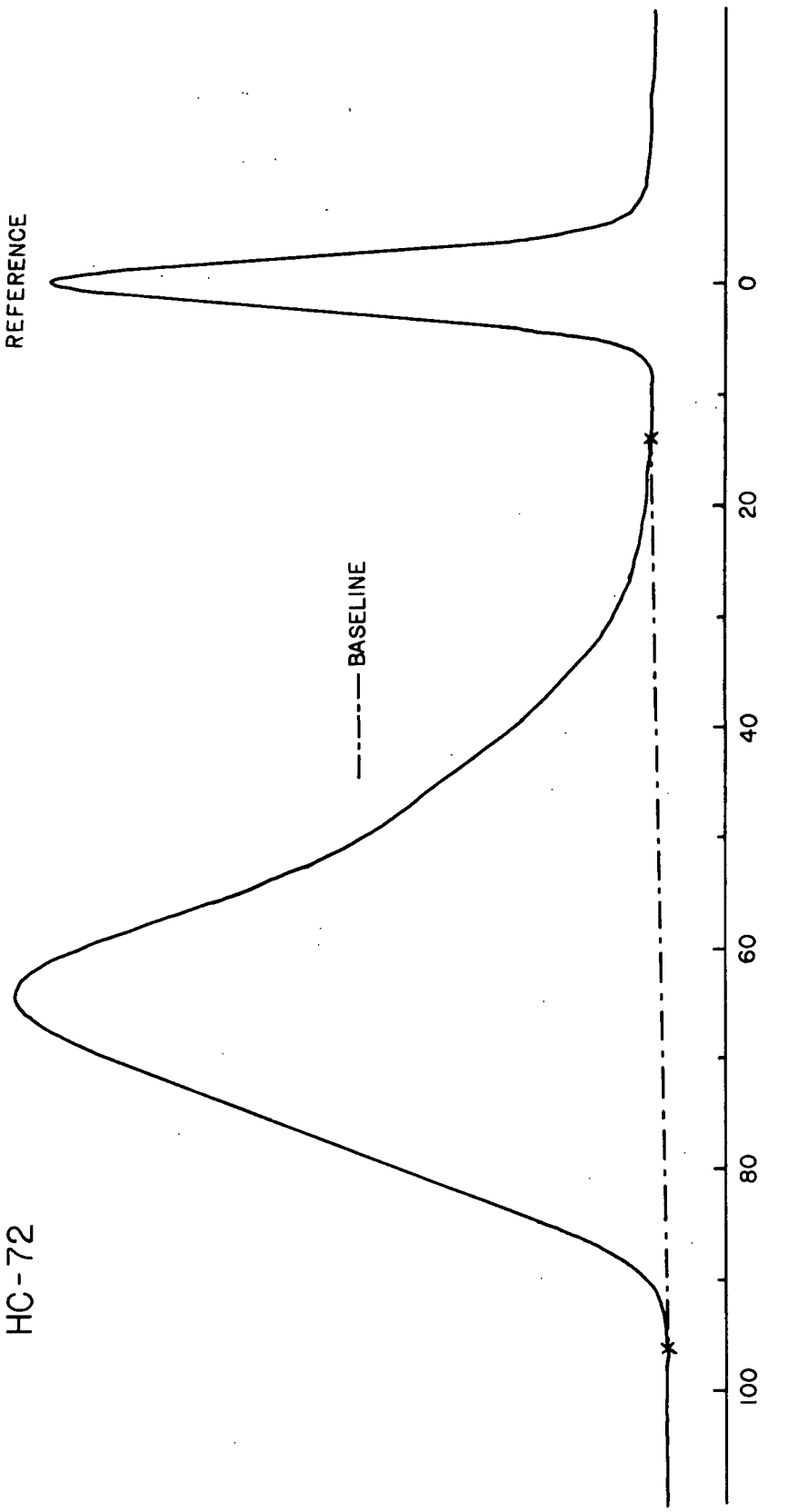


Figure 13. Gel Permeation Chromatogram Illustrating Baseline Definition

Because some baseline drift could occur, the baseline was defined as the line between a point on the elution curve at a $V_s - V_i$ value of 15 (d.p. $\tilde{=}$ 7) and the start of the polymer elution (see Fig. 13). The ordinate heights (h_i) relative to the baseline were then obtained at $V_s - V_i$ intervals of 2 ml for the entire elution curve. This provided at least 20 data points for the elution curve. The method of calculating the molecular weight and degree of polymerization from the values of h_i and $V_s - V_i$ is presented in the Results and Discussion section.

ACKNOWLEDGMENTS

The author gratefully acknowledges the assistance of F. C. Haigh and M. R. Eisold and helpful discussions with E. E. Dickey, J. W. Green, D. C. Johnson, G. A. Nicholls, R. A. Stratton, and N. S. Thompson. In addition, R. A. Stratton supplied several of the polystyrene standards used for GPC analyses. J. J. Bachhuber and J. O. Church provided assistance with computer operations.

LITERATURE CITED

1. Nicholls, G. A., IPC Funded Research Proposal, "Oxidative Delignification with Oxygen/Alkali To High-Yield Pulps," January 20, 1975.

2. Schroeder, L. R., IPC Funded Research Proposal, "Degradative Changes in Carbohydrates of Pulps from Oxygen-Alkali Reactions," June 9, 1975.

3. Meller, A., Holzforschung 14:78-89(1960).

4. Meller, A., Tappi 48:231-8(1965).

5. Whistler, R. L., and BeMiller, J. N., Adv. Carbohyd. Chem. 13:289-329(1958).

6. Rowell, R. M., Pulp Paper Mag. Can. 73:T236-9(1971).

7. Green, J. W. Project 3265, "Study of the Carbohydrate Peeling and Stopping Reactions Under the Conditions of Oxygen-Alkali Pulping," Report One, January 9, 1976.

8. Laver, M. L. and Zerrudo, J. V., Abstracts Fourth Canadian Wood Chemistry Symposium, July 4-6, 1973. p. 61.

9. Samuelson, O. and Sjöberg, L. A., Cellulose Chem. Technol. 8:39-48(1974).

10. Scholander, E., Durst, W. B., Pearce, G., and Dence, C. W., Tappi 57: 142-5(1974).

11. Chang, H., Gratzl, J. S., and McKean, W. T., Tappi 57:123-6(1974).

12. Marton, R. and Leopold, B., Appita 27:112-18(1973).

13. Ward, K., Jr., "Chemical Modification of Papermaking Fibers," Chapter 4, New York, Marcel Dekker, Inc., 1973.

14. Alince, B., Svensk Papperstidn. 78:253-6(1975).

15. Samuelson, O., Das Papier 24:671-8(1970).

16. Kolmodin, H. and Samuelson, O., Svensk Papperstidn. 73:93-6(1970).

17. Meller, A., Holzforschung 14:129-39(1960).

18. Nicholls, G. A., Jamieson, R. G., and Van Drunen, V. J., Tappi 58(5):105-9 (1975).

19. Matthews, C. H., Svensk Papperstidn. 77:629-35(1974).

20. Borchardt, L. G. and Piper, C. V., Tappi 53:257-60(1970).

21. Janson, J., Faserforsch. Textiletech. 25:375-82(1974).

22. Timell, T. E., Tappi 40:568-72(1957).

23. Sinkey, J. D. and Thompson, N. S., Paperi Puu 56:473-86(1974) and references therein.

24. Minor, J. L. and Sanyer, N., Tappi 57(5):120-2(1974).

25. Good, C. M., Reti, A. R., and Krongelb, M. S., American Laboratory 6 (10):71-8(1974).

26. Amicon Applications Manual No. 427A, Amicon Corporation, Lexington, MA, 1972.

27. Timell, T. E., Glaudemans, C. P. J., and Gillham, J. K., Tappi 42:623-34 (1959).

28. Spencer, F. S. and McLachlan, G. A., Plant Physiol. 49:58-63(1972).

29. Valtasaari, L. and Saarela, K., Paperi Puu 57:5-10(1975).

30. El Ashmawy, A. E., Danhelka, J., Kössler, I., Svensk Papperstidn. 77: 603-8(1974).

31. Grubisic, Z., Rempp, P., and Benoit, H., J. Polymer Sci. B5:753-9(1967) and references cited therein.

32. Detrick, R. W., Tappi 43:552-4(1960).

33. Johansson, M. H. and Samuelson, O., Carbohyd. Res. 34:33-43(1974).

34. Perrin, D. D., Armarego, W. L. F., and Perrin, D. R., Purification of Laboratory Chemicals, London, Pergamon Press. 1966.

35. Wolfrom, M. L. and Thompson, A., Methods Carbohyd. Chem. 2:211-15(1963).

36. MacDonald, D. L. and Fischer, H. O. L., J. Am. Chem. Soc. 77:4348-50(1955).

37. Hough, L. and Richardson, A. C. In Coffey, S. (ed.), Rodd's Chemistry of Carbon Compounds. Vol. I, part F, New York, Elsevier Publishing Company, 1967. p. 1-66.

38. Binkley, W. W. and Wolfrom, M. L., J. Am. Chem. Soc. 70:2809(1948).

39. Brimacombe, J. S. and Webber, J. M. In Pigman, W. and Horton, D. (eds.), The Carbohydrates, Vol. IA, New York, Academic Press, 1972. p. 478-518.

40. Lohmar, R. and Goepp, R. M., Jr., Adv. Carbohyd. Chem. 4:211-41(1949).

41. Langlois, D. P., Methods Carbohyd. Chem. 2:83-6(1963).

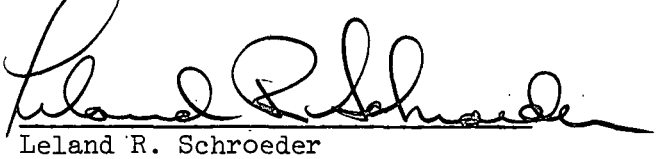
42. Wolfrom, M. L. and Thompson, A., Methods Carbohyd. Chem. 2:65-8(1963).

43. Schroeder, L. R., Green, J. W., and Johnson, D. C., J. Chem. Soc. (B) 1966:447-53.

44. Shriner, R. L., Fuson, R. C., and Curtain, D. Y., The Systematic Identification of Organic Compounds, 5th ed., New York, John Wiley and Sons, 1964. p. 316.

45. Holmes, G. W. and Kurth, E. F., Tappi 42:837-40(1959).

THE INSTITUTE OF PAPER CHEMISTRY



Leland R. Schroeder
Research Associate
Division of Natural
Materials & Systems